Journal of Power Sources 239 (2013) 356–360

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Performance of a direct methanol fuel cell using flexible proton-conducting glass-based composite membrane

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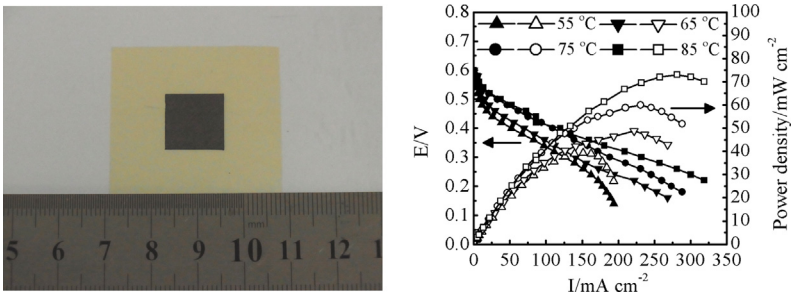
HIGHLIGHTS

- A direct methanol fuel cell with a composite membrane is prepared.
- The methanol permeability of the composite membrane is lower than that of Nafion®.
- The direct methanol fuel cell releases a peak power density of 73.1 mW cm^{-2}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form
25 March 2013
Accepted 26 March 2013
Available online 6 April 2013

Keywords:
Proton-conducting glass
Composite membrane
Direct methanol fuel cell
Cell performance

ABSTRACT

A direct methanol fuel cell (DMFC) with a proton-conducting composite membrane, which is synthesized from Nafion®/phosphosilicate (NPS) glass and sulfonated poly(ether ether ketone) (SPEEK) polymer, is prepared, and its performance is evaluated at different cell temperatures, methanol flow rates, and oxygen backpressures. The methanol permeability of the NPS/SPEEK composite membrane is determined to be 7.5 × 10^{-7} cm^2 s^{-1}. The developed DMFC releases a peak power density of 73.1 mW cm^{-2} at a cell temperature of 85 °C.

1. Introduction

Perfluorosulfonic polymer membranes, typically Nafion®, are characterized by high proton conductivity and good chemical stability, and are widely used as electrolytes in PEMFCs using hydrogen as fuel and DMFCs using methanol as fuel. However, these membranes are very expensive, and they suffer from swelling due to the adsorption of water and are, therefore, permeable to fuel, especially methanol. High methanol permeability through such membranes greatly lowers the efficiency of DMFCs, and represents one of the major barriers to the commercialization of DMFCs.

Much effort has been focused on exploring the possibilities of hydrocarbon-based membranes as low-cost candidates [1–6]. Among them, sulfonated poly(ether ether ketone) (SPEEK) is highly promising for use in DMFCs as it possesses superior thermal stability and high mechanical strength, is easily to handle, and shows adequate proton conductivity and low methanol permeability [4–6].

The composite membranes with inorganics have been developed. The addition of inorganic components into polymeric matrixes has the dual function of enhancing water retention and of

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http://dx.doi.org/10.1016/j.jpowsour.2013.03.147

providing additional acidic sites, so as to improve proton conductivity in elevated temperature range and low humidification level [7,8], and could reduce methanol permeability by a blocking effect [9]. On the other hand, sol–gel-derived inorganic proton conductors such as SiO_2 [10], TiO_2 [11], P_2O_5–SiO_2 [12,13], and P_2O_5–TiO_2 [14] is promising for the application in fuel cells, because of their low-cost, good dimensional stability, and high proton conductivity. However, the power densities of fuel cells with such inflexible inorganic proton-conductive membranes are not as high as those of fuel cells based on Nafion® membranes. It is believed that a key issue is that sol–gel-derived glasses are inflexible and fragile, and thus cannot withstand the pressure required to press them into a membrane-electrode assembly (MEA) for favorable interface contact between the electrolyte and electrode.

Based on Nafion®/phosphosilicate (NPS) glass and sulfonated poly(ether ether ketone) (SPEEK) polymer, our group has recently prepared glass-based NPS/SPEEK composite membranes by a simple mechanical ball-milling approach [15]. Due to the incorporation of the SPEEK polymer, the glass-based composite membranes exhibited sufficient flexibility and remarkably reduced pore volume compared to the fragile and highly porous NPS glass. It has been verified that an H_2/O_2 fuel cell equipped with the NPS/SPEEK composite membrane could release a peak power density of 322 mW cm^{-2} [15].

In this study, a single DMFC using methanol as fuel and based on the NPS/SPEEK composite membrane has been prepared, and its performance has been evaluated at different cell temperatures, anode flow rates, and cathode backpressures.

2. Experimental

2.1. Preparation of the NPS/SPEEK composite membrane

The preparation procedures, materials used, and the characterizations of the composite membrane can be found in Ref. [15].

2.2. Measurement of methanol permeability

Methanol permeability of the membranes was determined by using a two-chamber method. The membrane was clamped between the two chambers, the contents of which were stirred continuously during the experiments. One chamber contained pure deionized water (600 mL) and the other contained an 8 vol.% aqueous solution of methanol (600 mL). Samples were taken from the water chamber at intervals, and a gas chromatograph (GC-2010, Shimadzu) was used to determine their methanol concentrations.

The methanol permeability was calculated by the following equation:

$$C_B(t) = ADKC_A(t - t_0)/V_BL \quad (1)$$

where C_A and C_B are the methanol concentrations in the methanol chamber and in the water chamber; A and L are the effective area and thickness of the membrane; V_B is the volume of the water chamber; t is the permeation time; and D and K are the methanol diffusivity and partition coefficient, respectively. The product DK is the methanol permeability.

2.3. Preparation and characterization of DMFC

A single DMFC was prepared by using an NPS/SPEEK composite membrane with a thickness of 96 μm. Gas-diffusion electrodes (GDEs) with a Pt–Ru loading of 1.75 mg cm^{-2} as anode catalyst and a Pt loading of 1.75 mg cm^{-2} as cathode catalyst deposited on wet-proofed carbon papers were attached on both sides of the NPS/SPEEK composite membrane to form a sandwich structure. A membrane-electrode assembly (MEA) with an active area of 1.69 cm^2 (1.3 cm × 1.3 cm) was prepared by hot-pressing the sandwich structure under 0.3 MPa at 135 °C. The respective graphite blocks on the anode and cathode sides had a serpentine flow field with a width of 0.7 mm and a depth of 1 mm. Gold-coated copper plates were used as current collectors. The respective heating sheets were attached to aluminum end plates.

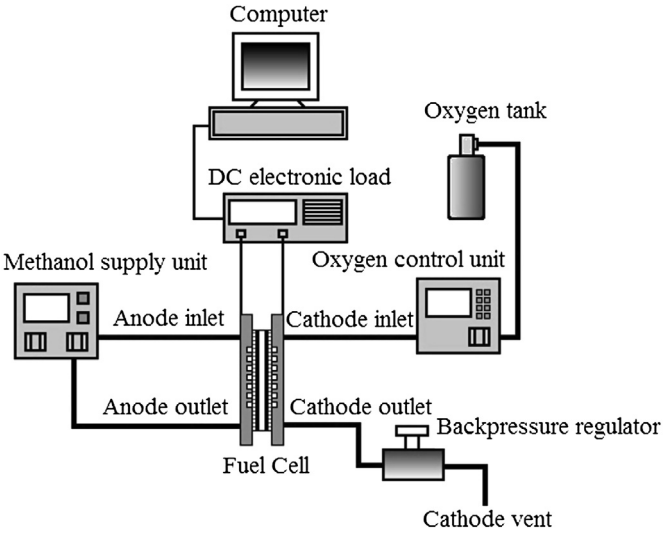

Fig. 1. Schematic layout of the DMFC testing apparatus.

The DMFC assembled with the above MEA was fed with methanol solution supplied to the anode and oxygen supplied to the cathode. The performance of the DMFC under various operating conditions was characterized by means of a fuel-cell testing system (MiniTest3000, Toyo Corp.) with a methanol supply unit. The layout of the DMFC testing apparatus is illustrated in Fig. 1. Details of the testing conditions are listed in Table 1.

3. Results and discussion

3.1. The NPS/SPEEK composite membrane, and its methanol permeation properties

An NPS/SPEEK composite membrane was prepared by mixing NPS glass powder and SPEEK polymer by a mechanical ball-milling approach. The NPS glass used had been synthesized by a sol–gel method from TEOS, H_3PO_4, and Nafion® solutions with a subsequent low-temperature hydrothermal treatment (below 150 °C), which prevented thermal degradation of the organic component. The obtained glass exhibited proton conductivities of the order of 10^{-2}–10^{-1} S cm^{-1} [13], comparable to those of commercially available Nafion® membranes. On the other hand, it is known that a high DS of SPEEK, with many hydrophilic groups, leads to high conductivity, but is associated with a greater susceptibility to swelling and fragility, while a low DS gives low conductivity, but high mechanical strength and thermal stability [16]. SPEEK with a DS of 65% was used for the preparation of the composite

Table 1
Experimental conditions.

Cell temperature	55, 65, 75, 85 °C
Anode flow rate	0.5, 2, 5 mL min^{-1}
Cathode backpressure	0.05, 0.1, 0.15, 0.2 MPa

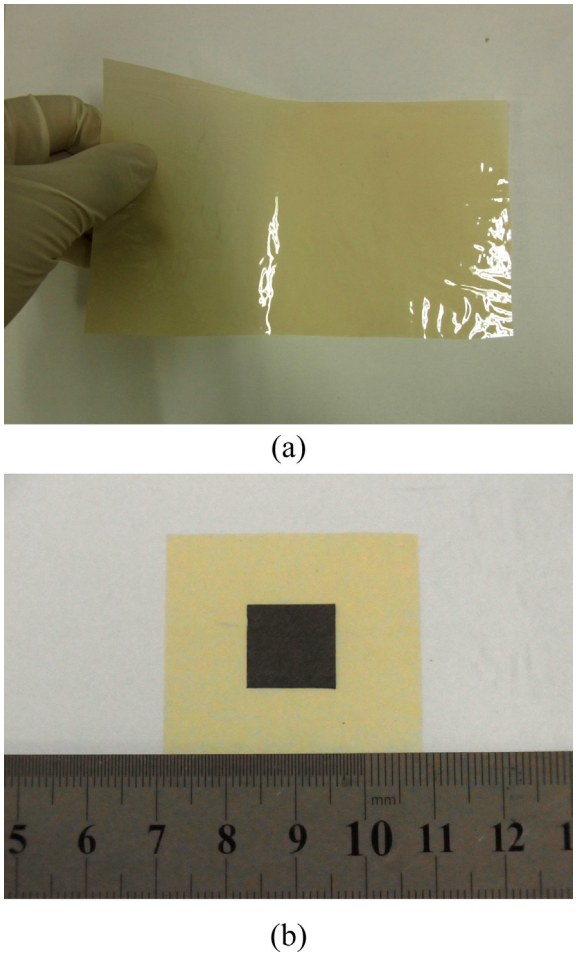

Fig. 2. Optical images of an NPS/SPEEK composite membrane (a), and an MEA with the NPS/SPEEK composite membrane (b).

membrane. In this study, we focused on the 6NPS/4SPEEK membrane consisting of NPS glass and SPEEK polymer in a weight ratio of 6:4, which has been reported to possess a proton conductivity of ca. 1×10^{-2} S cm^{-1}, and a tensile strength of 18 MPa [15].

Fig. 2(a, b) shows photographs of a 6NPS/4SPEEK composite membrane and an MEA with the NPS/SPEEK composite membrane, respectively. As can be seen in Fig. 2(a), the composite membrane had a yellowish, opaque appearance, and was smooth and crack-free, indicating that mechanical ball-milling is an efficient approach for preparing composite membranes consisting of glass powder and a polymer, even if the proportion of the glass component is as high as 60 wt.%. Fig. 2(b) shows that the MEA based on the 6NPS/4SPEEK composite membrane had a square active area of 1.3 cm × 1.3 cm.

In DMFCs, the permeation of methanol should be suppressed as much as possible, because if methanol fuel at the anode diffuses through the membrane to the cathode, it will react there, resulting in a mixed potential without generation of electricity. In an NPS/SPEEK composite membrane, the SPEEK component is promising for reducing methanol cross-over through the membrane, due to its narrower hydrophilic channels and greater branching compared with Nafion® [17]. Fig. 3 shows the methanol concentration that permeated through the NPS/SPEEK composite membrane as a function of time. The slope obtained from the linear relationship was used to calculate the methanol permeability according to Equation (1). The methanol permeability of the membrane was determined to be 7.5×10^{-7} cm^2 s^{-1}, which is lower than that of

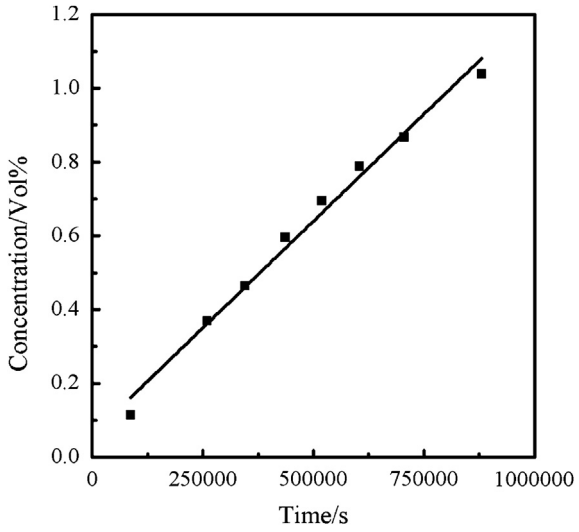

Fig. 3. Methanol concentration diffusing through the NPS/SPEEK composite membrane as a function of time.

2×10^{-6} cm^2 s^{-1} for a Nafion® membrane [18]. This may be attributed to the presence of the relatively impermeable SPEEK within the composite membrane adopted as a polymer matrix, and the incorporation of NPS glass powder particles as nano-scale reinforcements and fixtures that serve to restrain the swelling of the membrane body. Indeed, as previously reported, an NPS/SPEEK membrane has a small swelling ratio of 0.5% [15].

3.2. Effect of cell temperature on the DMFC performance

A single DMFC was assembled by using an MEA with an active area of 1.69 cm^2, which was prepared by hot-pressing of the NPS/SPEEK composite membrane, together with anode and cathode GDEs. This composite membrane could endure sufficient hot-pressing to assemble the MEA due to its good flexibility, so that good interfacial contacts between the electrolyte membrane and electrodes were formed.

The performance of the DMFC was characterized, and polarization and power output curves were recorded. To assess the effect of cell temperature on the performance of the DMFC, the

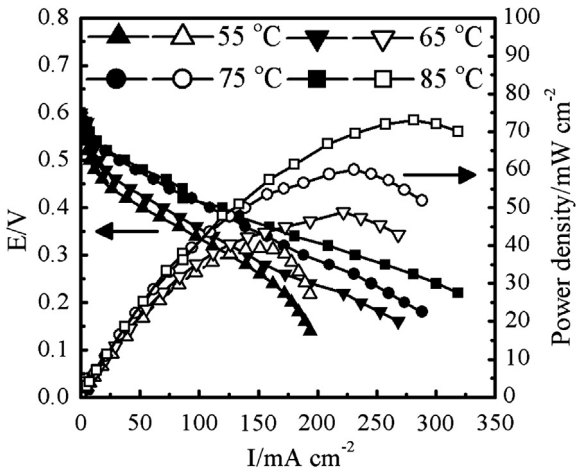

Fig. 4. The performances of a DMFC at 55 °C (a), 65 °C (b), 75 °C (c), and 85 °C (d) under operating conditions of a methanol concentration of 2 M, a methanol flow rate of 1 mL min^{-1}, an oxygen flow rate of 200 mL min^{-1}, and an oxygen backpressure of 0.2 MPa.

experimental cell temperature was increased from 55 to 85 °C in increments of 10 °C. As shown in Fig. 4, the DMFC had an open-circuit voltage of ca. 0.6 V at the various temperatures. As expected, the output power of the DMFC increased markedly with increasing cell temperature, with the peak power density increasing from 39.4 mW cm^{-2} at 55 °C to 73.1 mW cm^{-2} at 85 °C. This improvement of the DMFC performance with increasing cell temperature may be attributed to decreases in ohmic loss and activation loss. Ohmic loss can mainly be ascribed to the ohmic resistance of the composite membrane, and it decreases with increasing temperature. This may be attributed to an increase in membrane conductivity. For example, proton conductivities of ca. 4×10^{-3} S cm^{-1} at 30 °C and ca. 1×10^{-2} S cm^{-1} at 80 °C under 90% relative humidity have been reported in the literature [15]. Activation loss is derived from both anode and cathode polarizations. According to electrochemical reaction kinetics, increasing the temperature could increase the rate of the electrode reaction, and thereby decrease the activation loss [19]. In addition, an increased operation temperature could also improve the mass-transfer process, resulting in improved performance.

3.3. Effect of the methanol flow rate on DMFC performance

The effect of the methanol flow rate on the DMFC performance was evaluated. As shown in Fig. 5, the cell performance increased on increasing the methanol flow rate from 0.5 mL min^{-1} to 2 mL min^{-1}, but higher methanol flow rates had a negative effect. This can be rationalized in terms of increasing methanol flow rate enhancing the methanol transportation and providing a sufficient supply of methanol to the anode catalyst layer, but a higher methanol flow rate leading to an increase of methanol crossover through the composite membrane. In this study, the optimum value of the methanol flow rate was identified as 2 mL min^{-1}.

3.4. Effect of the cathode backpressure on the DMFC performance

Fig. 6 shows the effect of the oxygen backpressure on the DMFC performance at a cell temperature of 85 °C, as the oxygen backpressure was increased from 0.05 MPa to 0.2 MPa in 0.05 MPa intervals. It can be seen that the peak power density of the DMFC was 33.2 mW cm^{-2} at 0.05 MPa, which is much lower than the value at 0.2 MPa. The DMFC performance was obviously improved with

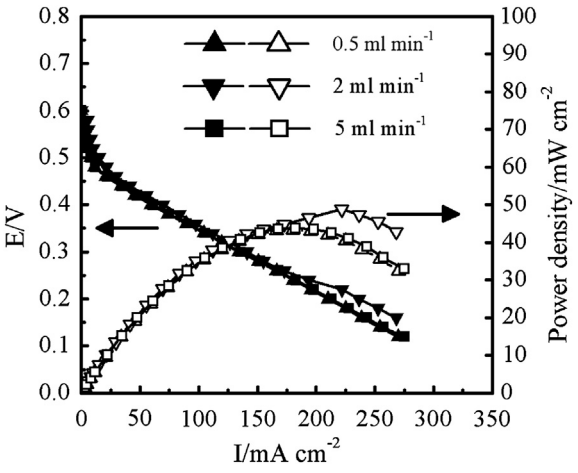

Fig. 5. The performances of a DMFC at various methanol flow rates of 0.5 mL min^{-1} (a), 2 mL min^{-1} (b), and 5 mL min^{-1} (c) at a cell temperature of 65 °C, a methanol concentration of 2 M, an oxygen flow rate of 200 mL min^{-1}, and a cathode backpressure of 0.1 MPa.

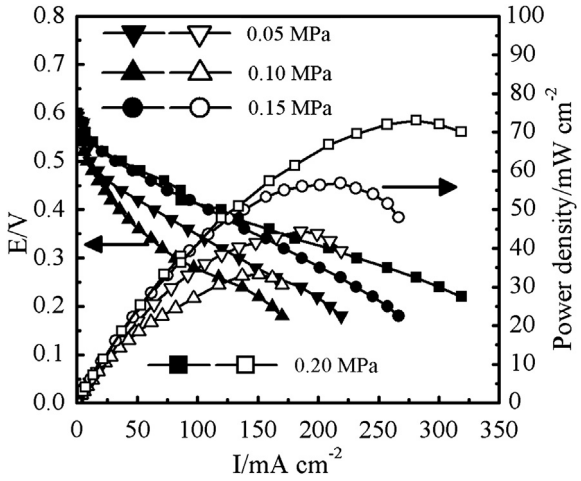

Fig. 6. Effect of the cathode backpressure on the performances of a DMFC at various oxygen backpressures of 0.05 MPa (a), 0.10 MPa (b), 0.15 MPa (c), and 0.20 MPa (d) at a cell temperature of 85 °C, a methanol concentration of 2 M, a methanol flow rate of 1 mL min^{-1}, and an oxygen flow rate of 200 mL min^{-1}.

increasing oxygen backpressure. It is suggested that methanol crossover was impeded by a decrease in electro-osmotic drag within the membrane under the increased oxygen backpressure, and that the reduction reaction at the cathode was enhanced by an increase in oxygen partial pressure [20]. In addition, increasing the oxygen backpressure may have enhanced the transportation of oxygen to the cathode catalyst layer, resulting in improvement of the DMFC performance.

4. Conclusion

In this study, a DMFC has been prepared with an NPS/SPEEK composite membrane consisting of NPS glass and SPEEK polymer, and its performance has been evaluated. A 6NPS/4SPEEK composite membrane with an NPS glass powder content of 60 wt.% was found to be flexible due to the incorporation of the SPEEK polymer component, and showed a low methanol permeability of 7.5×10^{-7} cm^2 s^{-1}. The developed DMFC released a peak power density of 73.1 mW cm^{-2} at a cell temperature of 85 °C. Based on the promising output power, such a low-cost, flexible composite membrane may possibly be used as an electrolyte in DMFCs.

Acknowledgments

This work was supported by the National High-Tech R&D Program (863 Program) (Grant no. 2009AA05Z113), and the National Natural Science Foundation of China (Grant no. 50672058).

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